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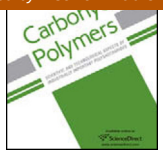

Effect of single and dual heat–moisture treatments on properties of rice, cassava, and pinhao starches

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ABSTRACT

The effects of single and dual heat–moisture treatment (HMT) of rice, cassava and pinhão starches at 100 °C and 120 °C were investigated. The starches were adjusted to 22% w.b. moisture content and subjected to single HMT (autoclaved for 2 h) or dual HMT (after being autoclaved for 1 h, the material was allowed to stand for 24 h and was autoclaved again for more 1 h). Starch crystallinity, solubility, swelling power, thermal properties, pasting properties, and gel hardness were evaluated. The temperature variation affected more the starch properties than the single or dual HMT. The starch subjected to single HMT at 120 °C was the most applicable to food applications, where low swelling power, low viscosity and high thermal stability are necessary.

1. Introduction

Starch is a semi-crystalline biopolymer that serves as a reserve carbohydrate in many plants, including seeds, roots, tubers and cereals. Starch is composed of amylose and amylopectin, and the ratio between these two macromolecules varies with the starch source analysed. Variations in the properties of starches from roots, tubers, seeds, cereals, and between varieties of a particular source of starch may be the result of differences in composition, morphology, molecular structure and arrangement of amylose and amylopectin within the starch granule (Hoover, 2010).

Starch, in its native form, has limited application in the industry. Therefore, starches are often modified by physical, chemical or enzymatic processes to provide specific functional properties. Physically modified starch can be considered as a natural material and a highly safe ingredient; therefore, the presence and quantity of the starch in food is not limited by legislation, which is considered a great advantage compared to chemical and enzymatic modified starches. Heat–moisture treatment (HMT) is defined as a physical modification that involves the treatment of the granules at a low moisture content (<35%) for a specific period of time (15 min–16 h) at temperatures (84–120 °C) above the glass transition and gelatinisation temperatures, in which the gelatinisation does not occur because of the poor moisture content of the HMT (Hoover, 2010). The HMT allows for the control of the molecular mobility at high temperatures by limiting the amount of water (Chung, Liu, & Hoover, 2009; Maache-Rezzoug, Zarguili, Loisel, Queveau, & Buléon, 2008). The HMT promotes a change in the structural arrangement of starch chains within the amorphous and crystalline areas of the granules, resulting in changes in granular swelling, crystallinity, amylose leaching parameters, gelatinisation, retrogradation, thermal stability and paste properties (Hoover, 2010).

Numerous studies have demonstrated the effects of HMT in starches from different sources, including rice (Hormdok & Noomhorm, 2007; Zavareze, Storck, Castro, Schirmer, & Dias, 2010), potato (Varatharajan et al., 2011; Vermeylen, Goderis, & Delcour, 2006), cassava (Gunaratne & Hoover, 2002), maize (Miyazaki & Morita, 2005; Pukkahuta, Suwannawat, Shobsngob, & Varavinit, 2008), canna (Watcharatewinkul, Puttanlek, Rungsardthong, & Uttapap, 2009) and pinhão (Pinto et al., 2012). Starches from different botanical sources have different responses to the conditions of HMT. Starches with standard X-ray type B crystalline structure have been shown to be more susceptible to treatment than starches with standard X-ray type A crystalline structure (Gunaratne & Hoover, 2002).

The effects of a single or dual hydrothermal treatment, using both the heat–moisture treatment followed by annealing (ANN) and the annealing followed by heat–moisture treatment, on the molecular structure and physicochemical properties of corn, pea, lentil, and navy bean starches have been reported (Chung et al.,

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2009; Chung, Liu, & Hoover, 2010). These authors reported that HMT, ANN–HMT and HMT–ANN were more effective than ANN in increasing thermal stability and decreasing the extent of setback.

The HMT promotes a pronounced effect on starch properties, and the treatment of dual HMT with a time interval between the treatments can provide a differentiated rearrangement in the molecular structure of the starch. However, there are no reports in the literature regarding the effect of dual HMT with combinations of different temperatures for rice, cassava and pinhão starches. The objective of this study was to evaluate the impact of single and dual HMT at different temperatures on the physicochemical properties of these starches.

2. Materials and methods

2.1. Materials

Rice grains of cultivars IRGA 417, provided by the Instituto Rio-Grandense do Arroz (IRGA), pinhão seeds (*Araucaria angustifolia* Bert O. Ktze) and cassava starch purchased in a local market in the city of Pelotas, Brazil, were used. The amylose content of rice, pinhão and cassava starches were 36.6, 26.9, 18.5% d.b., respectively. All reagents used were analytical grade.

2.2. Isolation of rice starch

Rice grains were dehulled, polished using a laboratory mill (model PAZ-1-DTA, Zaccaria, Limeira, Brazil) and ground using laboratory mill (Model 3100, Perten Instruments, Hägersten, Sweden) to obtain rice flour. Rice starch was isolated with 0.1% NaOH, as described by Wang and Wang (2004). Briefly, the rice flour was soaked in 0.1% NaOH in a 1:2 (w/v) ratio for 18 h. Then, the rice flour was blended, passed through a 63 μm screen and centrifuged at 1200 × *g* for 5 min. The soft top layer was carefully removed, and the underlying starch layer was re-slurried. The starch layer was then washed twice with 0.1% NaOH and centrifuged. The starch layer was washed with distilled water and centrifuged. The starch was then re-slurried and neutralised with 1.0 mol/L HCl to a pH of 6.5 and centrifuged. The neutralised starch was washed with distilled water three times and dried at 40 °C.

2.3. Isolation of Pinhão starch

The starch was isolated according to the method described by Bello-Pérez, García-Soarez, Méndez-Montealvo, Nascimento, and Cordenusi (2006) with some modifications. The pinhão seeds were dehulled and embedded in distilled water in a ratio of 1:2 (w/v). The material was ground in a laboratory blender for 5 min. The ground slurry was screened through a cotton cloth, and the filtered slurry was then passed through a 200-mesh sieve. The material remaining on the cloth and sieve was washed five times with distilled water. The filtrated slurry was allowed to stand for 5 h. Then, the starch was decanted and dried in an oven at 40 °C until the moisture content reached approximately 11%. The dried starch was ground using a laboratory mill (Model 3100, Perten Instruments, Hägersten, Sweden).

2.4. Heat–moisture treatment (HMT)

The heat–moisture treatment (HMT) of starches was performed according to the method described by Hormdok and Noomhorm (2007). The rice, cassava and pinhão starches were conditioned to 22% moisture for subsequent heat–moisture treatment. The amount of water needed to achieve the desired moisture content of the starch was added slowly with a burette and was mixed in a planetary mixer (Model K5SS, KitchenAid, St. Joseph, USA) for 15 min at low speed and equilibrated at 4 °C for 24 h. The samples were autoclaved at 100 °C or 120 °C for 2 h in the single step treatments (HMT 100 °C or 120 °C). In the dual treatments, the samples were autoclaved at 100 °C or 120 °C for 1 h, allowed to stand within the glass container for 24 h at 20° and again autoclaved at 100 °C or 120 °C for more 1 h (HMT-HMT 100 °C or 120 °C). The treated samples were subsequently dried at 40 °C in an oven and were then ground.

2.5. X-ray diffraction

X-ray diffractograms of the starches were obtained with a XRD-6000 (Shimadzu, Kyoto, Japan) diffractometer. The scanning region of the diffraction ranged from 5 to 45°, with a target voltage of 30 kV, a current of 30 mA and a scan speed of 1°/min. The relative crystallinity (RC) of the starch granules was calculated as described by Rabek (1980) using the equation $RC(\%) = (Ac/(Ac + Aa)) \times 100$, where *Ac* and *Aa* are the crystalline and amorphous areas, respectively.

2.6. Swelling power and solubility

The swelling power and solubility of the starches were determined as described by Leach, McCowen, and Schoch (1959). Samples (1.0 g) were mixed with 50 ml of distilled water in centrifuge tubes. The suspensions were heated at 90 °C for 30 min. The gelatinised samples were then cooled to room temperature and centrifuged at 1000 × *g* for 20 min. The supernatant was dried at 110 °C to constant weight to quantify the soluble fraction. The solubility was expressed as the percentage of dried solid weight based on the weight of the dry sample. The swelling power was represented as the ratio of the weight of the wet sediment to the weight of the initial dry sample less the amount of soluble starch.

2.7. Gel hardness

The gel texture profile was analysed with Texture Analyser (TA.XTplus, Stable Micro Systems Ltd., Godalming, UK) according to the method described by Hormdok and Noomhorm (2007) with some modifications. After taking the RVA measurement, the gelatinised mixture in the canister was stored at room temperature (20 °C) for 48 h, allowing the formation of a solid gel (3.0 g, 14% moisture content (wet basis)). The canister was sealed with parafilm to prevent moisture loss during storage. The gels were punctured at 1.0 mm/s to a distance of 10.0 mm using a stainless steel cylindrical probe (P/20, 20 mm diameter). The peak force measured was reported as the gel hardness (height of the first peak).

2.8. Pasting properties

The pasting properties of the starch samples (3.0 g for rice and pinhão starches and 2.5 g for cassava starch, 14% moisture basis) were determined by using a Rapid Visco Analyser (model RVA – 4, Newport Scientific, Australia) and profile Standard Analysis 1. Starch was weighed directly in the RVA-4 canister, and 25 mL of distilled water was then added. The sample was held at 50 °C for 1 min, heated to 95 °C in 3.5 min, and then held at 95 °C for 2.5 min. The sample was then cooled to 50 °C in 4 min and was held at 50 °C for 2 min. The rotating speed was held at 960 rpm for 10 s, and the speed was then maintained at 160 rpm during the process. Parameters including pasting temperature, peak viscosity, breakdown, final viscosity and setback were recorded.

2.9. Thermal properties

The gelatinisation characteristics of starches were determined using differential scanning calorimetry (DSC model 2010, TA

Instruments, New Castle, USA). Starch samples (approximately 2.5 mg, dry basis) were weighed directly in an aluminium pan, and distilled water was added to obtain a starch–water ratio of 1:3 (w/w). The pan was hermetically sealed and allowed to equilibrate for 1 h before analysis. The sample pans were then heated from 20 to 100 °C at a rate of 10 °C/min. An empty pan was used as a reference. The temperature at the onset of gelatinisation (To), the temperature at peak (Tp), the temperature at the end of gelatinisation (Tc) and the enthalpy (ΔH) of gelatinisation were determined. The temperature range of gelatinisation was calculated as Tc – To.

2.10. Statistical analysis

Analytical determinations for the samples were performed in triplicate, and standard deviations were reported, except the results of relative crystallinities and gelatinisation characteristics. A comparison of the means was ascertained by a Tukey's test to a 5% level of significance by analysis of the variance (ANOVA) using the Statistics 7.0 software.

3. Results and discussion

3.1. X-ray diffraction pattern and crystallinity

The X-ray diffractograms of native and modified rice, cassava and pinhão starches are presented in Fig. 1. The modified rice and cassava starches, with single and dual HMT, showed X-ray diffraction patterns similar to the respective native starches. The diffraction patterns are typical of A-type crystalline structure of starch as defined by the peaks at 2-theta = 15°, 17°, 17.8°, 19°, 23° and 28.5°. The native pinhão starch presented a C-type pattern (with diffraction peaks at 5.7°, 15°, 17°, 17.8° and 23°) (Fig. 1). The intensities of diffraction peaks and the relative crystallinity of native and HMT starches are presented in Table 1. The modified rice starches showed an increase in the intensities of the peaks of the single and dual HMT at 100 °C starches compared to the native one. When single and dual HMT at 120 °C were applied, there was a reduction of the peak intensities, except for the peaks at 2-theta = 19° and 2-theta = 28.5°. The HMT cassava starches showed higher peak intensities than the native cassava starch, except for the peak at 2-theta = 28.5°. There was a decrease in the peak intensities for all the HMT pinhão starches, except for the peak at 2-theta = 23° of single and dual HMT at 120 °C (Table 1). The native pinhão starch showed a peak at 2-theta = 5.7°, which is typical for C-type starches. However, when HMT was applied in the pinhão starch, the peak at 5.7° was not detected (Table 1). The increase in peak intensity after HMT has been reported in bean starch (Lawal & Adebowale, 2005) and wheat starch (Hoover & Vasanthan, 1994a), while the reduction in the peak intensities after HMT has been reported in potato starch (Lim, Chang, & Chung, 2001) and yam starch (Hoover & Vasanthan, 1994b).

Increase in intensities of diffraction peaks can be attributed to the structural rearrangement within the crystalline domain of the starch granules, where the moisture and thermal energy during HMT can promote the displacement of double helices between starch crystals, leading to the formation of a better packaged and ordered crystalline array than those from native starches (Hoover, 2010). The decrease in the X-ray peak intensity suggests a loss of the crystalline array, most likely because of broken hydrogen bonds, which can cause the displacement of the adjacent double helices and the rearrangement in orientations that are not in a perfect parallel array (Hoover & Vasanthan, 1994b). The decrease in X-ray peak intensities was observed mainly in A-type starches (rice and cassava), where the adjacent double helices within the starch crystals are linked by hydrogen bonds. According to Vermeylen et al. (2006), in B-type starches, the double helices present both a lateral and a hexagonal movement when subjected to HMT, losing the initial diffraction peak at 2-theta = 5.7° and, thus, changing its pattern from B-type to A-type. This explains the disappearance of the diffraction peak at 2-theta = 5.7° in native pinhão starch when

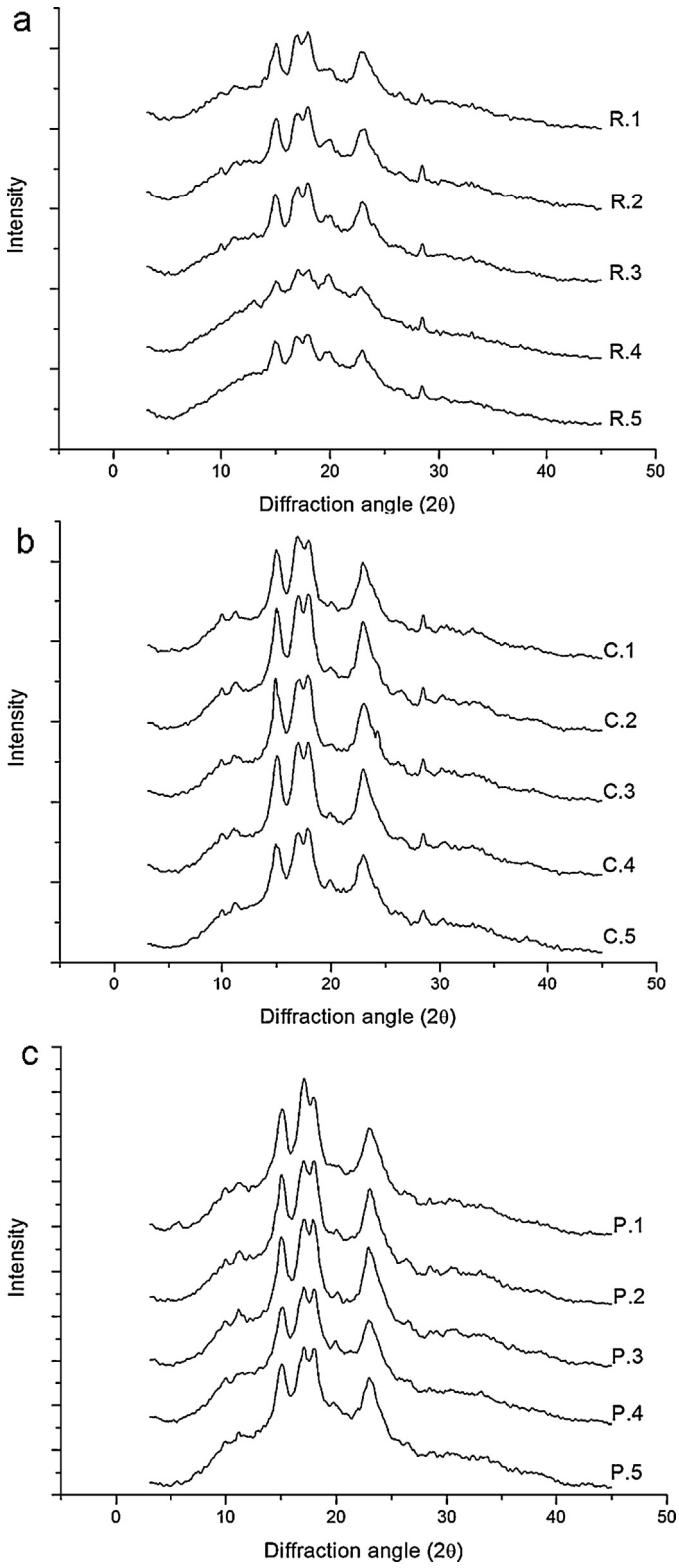

Fig. 1. X-ray diffractograms of native and HMT rice (a), cassava (b) and pinhão (c) starches. The numbers after the letters R (for rice), C (for cassava) and P (for pinhão) represent: 1 – native starch; 2 – single HMT at 100 °C; 3 – dual HMT at 100 °C; 4 – single HMT at 120 °C; 5 – dual HMT at 120 °C.

Table 1
Peak intensities from X-ray diffractograms and relative crystallinity of native and HMT rice, cassava and pinhão starches.

Starch source	Treatments[a]	Peak intensities						RC (%)[b]
		15.0°	17.0°	17.8°	19.0°	23.0°	28.5°	
Rice	Native	1409	1522	1542	1111	1330	801	38.6
	Single HMT at 100 °C	1477	1539	1636	1208	1346	906	35.5
	Dual HMT at 100 °C	1491	1573	1596	1206	1389	866	36.3
	Single HMT at 120 °C	1372	1511	1498	1438	1281	972	24.2
	Dual HMT at 120 °C	1440	1456	1509	1272	1313	856	24.0
		15.0°	17.0°	17.8°	19.0°	23.0°	28.5°	
Cassava	Native	1007	1768	1929	1883	1560	1003	39.5
	Single HMT at 100 °C	1047	2006	2144	2186	1721	1005	38.9
	Dual HMT at 100 °C	1010	1781	1952	1972	1644	953	39.2
	Single HMT at 120 °C	1049	1920	2091	2082	1786	987	30.7
	Dual HMT at 120 °C	1031	1782	1930	1953	1622	958	29.6
		5.7°	15.0°	17.0°	18.0°	23.0°		
Pinhão	Native	605	1854	2201	1965	1257		39.8
	Single HMT at 100 °C	nd[c]	1477	1539	1636	1208		38.5
	Dual HMT at 100 °C	nd	1491	1573	1596	1206		38.9
	Single HMT at 120 °C	nd	1372	1511	1498	1438		32.7
	Dual HMT at 120 °C	nd	1440	1456	1509	1279		33.8

[a] HMT, heat–moisture treatment.
[b] RC, relative crystallinity.
[c] nd, non-detected.

HMT was applied. C-type is a mixture of A- and B-type crystalline structures. Thus HMT changed the crystalline structure of native pinhão starch from C- to A-type (Fig. 1).

The single and dual HMT reduced the relative crystallinity of rice, cassava and pinhão starches compared to its respective native starches (Table 1). Zavareze et al. (2010) also reported a reduction in the relative crystallinity of rice subjected to HMT, as well as Chung et al. (2010), who observed a decrease in the relative crystallinity of pea, lentil and bean starches when subjected to HMT at 120 °C and 30% moisture content. The strongest reductions were observed in the single and dual HMT at 120 °C (Table 1). Thus, the dual HMT did not intensify the rupture of amylopectin crystals, but the highest temperature used during HMT promoted a destabilisation of the lamellar array, leading to a decrease in relative crystallinity.

3.2. Swelling power and solubility

The swelling power and solubility of native and HMT rice, cassava and pinhão starches are presented in Table 2. The native cassava starch showed a higher swelling power than native rice and pinhão starches. The swelling power is primarily a property of amylopectin, where amylose is considered a diluent (Hoover, 2010). In our study, the rice starch amylose comprises approximately 36.9%, whereas the cassava and pinhão starches presented 26.9% and 18.5% of amylose content, respectively. Thus, the cassava starch shows the highest swelling power because of its higher amylopectin content than rice and pinhão starches.

There was a decrease in the swelling power of rice starch with the increase in HMT temperature, considering the increase from 100 to 120 °C used in single and dual HMT (Table 2). Analysing the HMT rice starches, the swelling power reduction was more intensive when dual HMT at 120 °C was applied (Table 2). The swelling power of cassava and pinhão starches has also decreased as a function of single and dual HMT compared to their respective native starches; however, the swelling power of single and dual HMT at the same temperature was not significantly different (Table 2). Thus, it is possible to infer that the rice starch was more susceptible to a new arrangement caused by dual HMT at 120 °C, while the cassava and the pinhão starches were more susceptible to the temperature increasing from 100 to 120 °C during HMT. These results are in accordance to those reported by Hormdok and Noomhorm (2007), who observed a decrease in the swelling power of rice starch subjected to HMT under different moisture and temperature levels compared to native rice starch. Moreover, Gunaratne

Table 2
Swelling power, solubility, and gel hardness of native and HMT rice, cassava and pinhão starches.

Starch source	Treatments[a]	Swelling power (g/g)	Solubility (%)	Gel hardness (N)
Rice	Native	15.02 ± 0.46 a[b]	7.93 ± 0.35 a	3.38 ± 0.18 c
	Single HMT at 100 °C	14.07 ± 0.19 b	6.99 ± 0.33 b	3.99 ± 0.09 b
	Dual HMT at 100 °C	11.56 ± 0.38 c	6.53 ± 0.24 bc	4.82 ± 0.22 a
	Single HMT at 120 °C	11.10 ± 0.12 c	6.36 ± 0.09 c	1.91 ± 0.07 e
	Dual HMT at 120 °C	8.80 ± 0.06 d	5.42 ± 0.24 d	2.57 ± 0.18 d
Cassava	Native	29.11 ± 0.08 a	25.66 ± 0.18 a	0.70 ± 0.03 b
	Single HMT at 100 °C	17.80 ± 0.38 b	17.17 ± 0.05 b	1.70 ± 0.01 a
	Dual HMT at 100 °C	17.58 ± 0.22 b	12.50 ± 0.26 c	1.68 ± 0.07 a
	Single HMT at 120 °C	13.57 ± 0.01 c	11.07 ± 0.18 d	1.64 ± 0.20 a
	Dual HMT at 120 °C	13.82 ± 0.07 c	10.70 ± 0.13 d	1.56 ± 0.08 a
Pinhão	Native	14.61 ± 0.13 a	11.40 ± 0.16 a	4.71 ± 0.20 c
	Single HMT at 100 °C	12.22 ± 0.17 b	4.40 ± 0.21 d	7.43 ± 0.56 a
	Dual HMT at 100 °C	12.44 ± 0.29 b	5.01 ± 0.24 c	7.17 ± 0.43 a
	Single HMT at 120 °C	10.87 ± 0.19 c	5.47 ± 0.04 b	5.54 ± 0.17 b
	Dual HMT at 120 °C	10.56 ± 0.16 c	5.67 ± 0.05 b	4.49 ± 0.12 c

[a] HMT: heat–moisture treatment.
[b] The results are the means of three replications ± standard deviations. For each starch source, data entries in the same column followed by different letters differ significantly ($P < 0.05$).

Table 3
Pasting properties of native and HMT rice, cassava and pinhão starches.

Starch source	Treatments[a]	Pasting temperature (°C)	Peak viscosity (RVU)	Breakdown (RVU)	Setback (RVU)	Final viscosity (RVU)
Rice	Native	64.0 ± 0.8 d[b]	253.1 ± 0.7 a	44.1 ± 0.9 b	95.0 ± 1.8 a	304.3 ± 3.1 a
	Single HMT at 100 °C	71.6 ± 0.3 bc	230.0 ± 0.7 b	65.1 ± 2.7 a	87.3 ± 2.3 b	248.5 ± 0.9 c
	Dual HMT at 100 °C	70.2 ± 0.1 c	216.7 ± 1.2 c	34.6 ± 4.0 c	95.5 ± 2.1 a	281.6 ± 1.0 b
	Single HMT at 120 °C	72.6 ± 2.2 abc	133.9 ± 1.4 e	22.4 ± 1.0 d	29.7 ± 0.8 d	141.2 ± 1.9 e
	Dual HMT at 120 °C	75.3 ± 1.3 a	189.4 ± 0.1 d	40.8 ± 0.2 b	59.3 ± 0.3 c	207.8 ± 0.3 d
Cassava	Native	64.5 ± 0.1 c	364.3 ± 1.5 a	215.8 ± 0.7 a	69.6 ± 2.3 d	215.0 ± 1.6 d
	Single HMT at 100 °C	68.5 ± 0.1 ab	301.3 ± 5.4 b	103.0 ± 1.7 c	88.0 ± 1.3 b	283.7 ± 4.4 a
	Dual HMT at 100 °C	69.5 ± 1.3 a	274.0 ± 3.6 c	86.7 ± 2.1 d	93.6 ± 2.8 a	285.3 ± 1.6 a
	Single HMT at 120 °C	67.4 ± 0.4 b	218.7 ± 2.7 e	86.7 ± 0.6 d	84.5 ± 0.6 c	225.0 ± 4.1 c
	Dual HMT at 120 °C	68.6 ± 0.1 ab	260.0 ± 0.3 d	113.5 ± 2.2 b	91.9 ± 0.4 a	238.5 ± 2.3 b
Pinhão	Native	64.6 ± 0.1 c	356.6 ± 2.2 a	182.2 ± 0.7 a	83.0 ± 0.9 c	256.4 ± 2.5 d
	Single HMT at 100 °C	71.6 ± 0.9 b	210.2 ± 1.6 b	24.5 ± 2.0 d	161.5 ± 1.8 a	342.0 ± 3.0 a
	Dual HMT at 100 °C	70.5 ± 0.4 b	194.5 ± 1.5 c	35.6 ± 2.0 c	163.7 ± 5.7 a	328.0 ± 5.9 b
	Single HMT at 120 °C	75.6 ± 0.5 a	193.2 ± 0.2 c	40.9 ± 2.4 b	134.4 ± 4.5 b	284.3 ± 3.5 c
	Dual HMT at 120 °C	76.4 ± 0.4 a	164.5 ± 2.6 d	31.6 ± 2.7 c	128.3 ± 1.8 b	261.2 ± 5.8 d

[a] HMT: heat–moisture treatment.
[b] The results are the means of three replications ± standard deviations. For each starch source, data entries in the same column followed by different letters differ significantly ($P < 0.05$).

and Hoover (2002) and Pinto et al. (2012) verified a decrease in the swelling power of HMT cassava and pinhão starches, respectively, compared to their native starches. According to Zavareze and Dias (2011), loss in swelling power of starch following HMT can be attributed to increased amylose–amylopectin interaction, stronger intramolecular bonding, formation of amylose–lipid complexes, or alteration of the crystalline array of starch.

The highest solubility values were observed in the native starches and were ordered as follows: cassava > pinhão > rice (Table 2). The starch solubility is a result of amylose leaching, which dissociates and diffuses out of the starch granule during swelling. HMT reduced the solubility of rice, cassava and pinhão starches. The rice starch showed the lowest solubility when treated with dual HMT at 120 °C, while the cassava starch presented the lowest solubility when treated with single at 120 °C and dual HMT at 120 °C (are not significantly different), and the pinhão starch presented the lowest solubility when treated with single HMT at 100 °C (Table 2). The decrease in starch solubility can be attributed to an internal rearrangement of starch granules that provides higher interactions between starch functional groups, the formation of more ordered amylopectin clusters, and the formation of amylose-lipid complexes within starch granule (Zavareze & Dias, 2011). Thus, the poor amylose leaching of rice starch, considering its high amylose content, can be reflected in the strong interaction between amylose–amylose and amylose–amylopectin, complicating the leaching from starch granules. Similar results were reported in pea, lentil and bean starches (Chung et al., 2010), rice starch (Zavareze et al., 2010), and yam and potato starches (Gunaratne & Hoover, 2002).

3.3. Gel hardness

The gel hardness of native and HMT rice, cassava and pinhão starches is presented in Table 2. The highest gel hardness, considering native and HMT starches, was found in pinhão starch, followed by rice and cassava starches. The gel hardness is caused mainly by starch retrogradation, which is more influenced by amylose presence than amylopectin. Thus, the higher gel hardness observed in HMT pinhão starch has most likely occurred because of its lower solubility (amylose leaching) compared to the other studied starch sources (Table 2), which leads to a higher setback. The HMT cassava starches showed a higher gel hardness than the native cassava starch, but there was no difference as a function of single or dual HMT and/or temperature used. Single and dual HMT at 100 °C increased the gel hardness of rice starch, while single and dual HMT at 120 °C reduced the gel hardness of rice starch compared to native rice starch. This decrease in gel hardness suggests a partial gelatinisation of starch when the highest temperature of our study was applied (120 °C). This phenomenon provides a collapse of starch structure and, thus, a less rigid gel. From Table 2, changes that occurred in rice and pinhão starches were more influenced by the temperature HMT rather than the number of treatment times, that is, single or dual HMT Similar results were reported by Hormdok and Noomhorm (2007), who observed an increase in the gel hardness of rice starch when subjected to HMT. Pinto et al. (2012) also reported an increase in the gel hardness of pinhão starch subjected to HMT. This increase in gel hardness can be attributed to an increase in cross-links between starch chains, in particular in the amylose fraction, which leads to a larger junction area in the continuous phase of the gel (Liu, Corke, & Ramsden, 2000).

3.4. Pasting properties

The pasting properties of native and HMT rice, cassava and pinhão starches are presented in Table 3. Changes in the pasting properties as a function of HMT have been attributed to a decrease in the granular swelling and amylose leaching and an increase in the interactions between starch chains and granular rigidity (Hoover, 2010).

The paste properties are shown as changes in viscosity during the heating of a suspension of starch and reflect changes in the physical and chemical structure of starch. The pasting temperature is related with the initiation of paste formation. The native starches showed similar pasting temperatures (Table 3). Single and dual HMT at 100 °C and 120 °C increased the pasting temperature of rice, cassava and pinhão starch. Higher pasting temperatures observed in HMT starches suggest that more forces and cross-links are present within the starch granule that requires a higher heating temperature for structural breakdown and paste formation (Zavareze & Dias, 2011). The higher pasting temperature in HMT starches compared to the native starches corresponds to increased gelatinisation temperatures.

In general, there was a reduction in the peak viscosity of all starch sources studied with the increase in HMT temperature and with the application of dual HMT compared to the respective native starches, except when dual HMT at 120 °C was used for rice and cassava starches (Table 3). The highest peak viscosity presented by cassava starch can be related with its higher swelling power compared to rice and pinhão starches. Swelling power promotes the hydration of amorphous lamellae, thus high swelling power

Table 4
Thermal properties of native and HMT rice, cassava and pinhão starches.

Starch source	Treatments[a]	Gelatinisation temperatures[b]			Tc – To (°C)	Enthalpy (J/g)
		To (°C)	Tp (°C)	Tc (°C)		
Rice	Native	57.46	62.12	67.93	10.47	11.85
	Single HMT at 100 °C	70.62	73.07	76.10	5.48	6.10
	Dual HMT at 100 °C	69.85	73.14	75.73	5.88	6.78
	Single HMT at 120 °C	63.51	70.40	73.77	10.26	1.68
	Dual HMT at 120 °C	75.69	78.83	81.94	6.25	0.73
Cassava	Native	63.00	68.01	73.96	10.96	13.98
	Single HMT at 100 °C	70.67	74.45	78.77	8.10	9.18
	Dual HMT at 100 °C	69.61	75.27	80.07	10.46	10.98
	Single HMT at 120 °C	70.14	74.96	78.41	8.27	4.63
	Dual HMT at 120 °C	72.50	78.53	81.86	9.36	5.92
Pinhão	Native	60.73	66.69	72.77	12.04	15.54
	Single HMT at 100 °C	70.92	74.36	77.70	6.78	3.37
	Dual HMT at 100 °C	70.64	75.23	78.71	8.07	4.84
	Single HMT at 120 °C	65.80	80.61	84.83	19.03	5.66
	Dual HMT at 120 °C	65.36	81.35	84.86	19.50	6.97

[a] HMT, heat–moisture treatment.
[b] To, onset temperature; Tp, peak temperature; Tc, conclusion temperature.

coincides with high peak viscosities. The decrease in peak viscosity as affected by the increase in HMT temperature was also observed by Pinto et al. (2012) in HMT pinhão starch. However, the association between the temperature and single or dual HMT resulted in distinct effects in rice, cassava and pinhão starches. In rice and cassava starches subjected to HMT, the lowest peak viscosity values were verified in single HMT at 120 °C, while the pinhão starch showed its lowest peak viscosity value where treated with dual HMT at 120 °C.

The single and dual HMT of rice, cassava and pinhão starches decreased starch viscosity breakdown, except for rice starch subjected to single HMT at 100 °C. The decrease in starch breakdown indicates the high stability of these starches while subjected to heating and mechanical agitation, which is in accordance to Pinto et al. (2012), Zavareze et al. (2010), and Hormdok and Noomhorm (2007). Single HMT at 120 °C caused the highest decrease in viscosity breakdown in rice starch. In cassava starch, both dual HMT at 100 °C and single HMT at 120 °C promoted the greatest decrease in viscosity breakdown. Pinhão starch, on the other hand, showed the highest viscosity breakdown decrease when subjected to single HMT at 100 °C.

The setback is influenced by amylose leaching, granule size and presence of non-fragmented swollen granules (Lan et al., 2008). Comparing only the native starches, the highest setback was observed in rice starch, followed by pinhão and cassava starches. Another factor that can influence starch setback is amylose content. Amylose has greater ability to rearrange after gelatinisation. As cassava starch presents the lowest amylose content compared to rice and pinhão starches, it showed the lowest setback. The HMT pinhão starches showed higher setback values than rice and cassava HMT starches. As the setback is also influenced by amylose leaching, the increase in setback of HMT pinhão starches can be associated to the solubility decrease observed for this starch after HMT.

Highest final viscosity was observed in rice starch, followed by pinhão starch. Cassava starch had the lowest final viscosity. The final viscosities of HMT rice starches were lower than the final viscosity of native rice starch, while the final viscosities of cassava and pinhão starches increased with single and dual HMT at 100 °C and decreased with single and dual HMT at 120 °C; however, even with this final reduction of viscosity when dual HMT at 120 °C was applied, the final viscosity was still greater than those from their respectives native starch. Because the final viscosity indicates the ability of starch to form a viscous paste, this property can be related to the gel hardness of studied starches, where cassava starch, generally, had lower gel hardness compared to rice and pinhão starches. The increase in final viscosity was accompanied by an increase in the gel hardness in HMT pinhão and cassava starches.

3.5. Thermal properties

The thermal properties of native and HMT rice, cassava and pinhão starches are presented in Table 4. The native cassava starch showed the highest gelatinisation temperatures, followed by pinhão and rice starches. HMT increased the onset temperature (To), the peak temperature (Tp) and the conclusion temperature (Tc) of rice, cassava and pinhão starches. Adebowale, Henle, Schwarzenbolz, and Doert (2009) also observed higher To, Tp and Tc in African bean starch subjected to HMT at different moisture levels. The increase in To, Tp and Tc is attributed to structural changes within starch granule, which involves amylose–amylose and amylose–lipid interactions, repressing the mobility of starch chains within amorphous lamellaes (Hoover, 2010). The increase in the peak gelatinisation temperature in case of dual treatment also may be due to formation of resistant starch. The To of rice starch subjected to single HMT at 120 °C and the To of pinhão starches subjected to single and dual HMT at 120 °C were lower than the To from their respectives single and dual HMT at 100 °C. This suggests that the higher mobility of starch chains at 120 °C possibly does not allow the expected increase in To by reducing the extent of interactions between amylose–amylopectin and amylopectin–amylopectin chains. Similar results were reported by Varatharajan et al. (2011), for normal and waxy potato starches. The highest Tc – To between the native starches was observed in pinhão starch. The HMT resulted in a reduction of the Tc – To in the three studied sources, except for the pinhão starch treated with both single and dual HMT at 120 °C. The increase in Tc – To indicates that the HMT allows the formation of new starch crystallites with different thermal stabilities. Pinto et al. (2012) also observed a higher Tc – To in HMT pinhão starch compared to the native pinhão starch.

The gelatinisation enthalpy of the native starches followed the order pinhão > cassava > rice. HMT reduced gelatinisation enthalpy of the starches (Table 4). Similar observations were also reported by Adebowale et al. (2009) for heat–moisture treated African bean starch. The decrease in enthalpy may be attributed to disruption of double helices in the crystalline and amorphous lamellaes of the starch granule or partial gelatinisation of less stable amylose and amylopectin molecules during heating (Zavareze & Dias, 2011). The

effect of the displacement of double helices between starch crystals, which forms a weaker ordered crystalline matrix, was more pronounced in single and dual HMT at 120 °C for rice and cassava starches. These results can also be due to formation of new starch crystals that must present different thermal stabilities in single and dual HMT at 120 °C starches, leading to a high energy requirement for the dissociation of the new crystals.

4. Conclusions

HMT promoted changes in peak intensities and relative crystallinity from X-ray diffractograms. The greatest reduction in relative crystallinity was observed in the HMT of rice at 120 °C. Pinhão starch changed from C-type pattern to an A-type pattern when subjected to HMT.

The swelling power of dual HMT starches was different from the single HMT for rice starch only. Normally, HMT promotes an increase in gel hardness and a decrease in solubility, as a function of enhanced cross-linking between starch chains; however, single and dual HMT at 120 °C seems to promote a partial gelatinisation of rice starch, reducing rice starch gel hardness, setback and final viscosity by 43.5%, 68.7% and 53.6%, respectively, when single HMT at 120 °C was applied. The partial gelatinisation occurance is also supported by gelatinisation enthalpy, where the greatest reduction was observed for rice starch. The pinhão starch subjected to single and dual HMT at 120 °C presented a reduction in the gel hardness compared to pinhão starch treated at 100 °C, suggesting a partial collapse of the starch crystalline structure at this temperature; however, the gelatinisation temperature range (Tc – To) of pinhão starch treated with single and dual HMT at 120 °C increased approximately 58.3% compared to the native pinhão starch, indicating the formation of new starch crystallites with different thermal stabilities. The increase in the peak gelatinisation temperature in case of dual treatment may be due to formation of resistant starch.

The starch subjected to single HMT at 120 °C is the most applicable to food applications, where low swelling power, low viscosity and high thermal stability are necessary, mainly when rice starch is the available source.

References

Adebowale, K. O., Henle, T., Schwarzenbolz, U., & Doert, T. (2009). Modification and properties of African yam bean (*Sphenostylis stenocarpa* Hochst. Ex A. Rich.) Harms starch I: Heat moisture treatments and annealing. *Food Hydrocolloids*, *23*, 1947–1957.

Bello-Pérez, L. A., García-Soarez, F. J., Méndez-Montealvo, G., Nascimento, J. R. O., & Cordenusi, B. R. (2006). Isolation and characterization of starch from seeds of *Araucaria brasiliensis*: A novel starch for application in food industry. *Starch/Starke*, *58*, 283–291.

Chung, H. J., Liu, Q., & Hoover, R. (2009). The impact of single and dual hydrothermal modifications on the molecular structure and physicochemical properties of normal corn starch. *International Journal of Biological Macromolecules*, *44*, 203–210.

Chung, H. J., Liu, Q., & Hoover, R. (2010). Effect of single and dual hydrothermal treatments on the crystalline structure, thermal properties, and nutritional fractions of pea, lentil, and navy bean starches. *Food Research International*, *43*, 501–508.

Gunaratne, A., & Hoover, R. (2002). Effect of heat–moisture treatment on the structure and physicochemical properties of tuber and root starches. *Carbohydrate Polymers*, *49*, 425–437.

Hoover, R. (2010). The impact of heat–moisture treatment on molecular structures and properties of starches isolated from different botanical sources. *Critical Reviews in Food Science and Nutrition*, *50*, 835–847.

Hoover, R., & Vasanthan, T. (1994a). The flow properties of native, heat–moisture treated and annealed starches from wheat, oat, potato and lentil. *Journal of Food Biochemistry*, *18*, 67–82.

Hoover, R., & Vasanthan, T. (1994b). Effect of heat–moisture treatment on the structure and physicochemical properties of cereal, legume, and tuber starches. *Carbohydrate Research*, *252*, 33–53.

Hormdok, R., & Noomhorm, A. (2007). Hydrothermal treatments of rice starch for improvement of rice noodle quality. *LWT-Food Science and Technology*, *40*, 1723–1731.

Lan, H., Hoover, R., Jayakody, L., Liu, Q., Donner, E., Baga, M., et al. (2008). Impact of annealing on the molecular structure and physicochemical properties of normal, waxy and high amylose bread wheat starches. *Food Chemistry*, *111*, 663–675.

Lawal, O. S., & Adebowale, K. O. (2005). An assessment of changes in termal and physicochemical parameters of jack bean (*Canavalia ensiformis*) starch following hydrothermal modifications. *European Food Research Technology*, *221*, 631–638.

Leach, H. W., McCowen, L. D., & Schoch, T. J. (1959). Structure of the starch granule. I. Swelling and solubility patterns of various starches. *Cereal Chemistry*, *36*, 534–544.

Lim, S. T., Chang, E. H., & Chung, H. J. (2001). Thermal transitions characteristic of heat–moisture treated corn and potato starches. *Carbohydrate Polymers*, *46*, 107–115.

Liu, H., Corke, H., & Ramsden, L. (2000). The effect of autoclaving on the acetylation of ae, wx and normal maize starches. *Starch/Stärke*, *52*, 353–360.

Maache-Rezzoug, Z., Zarguili, I., Loisel, C., Queveau, D., & Buléon, A. (2008). Structural modifications and thermal transitions of standard maize starch after DIC hydrothermal treatment. *Carbohydrate Polymers*, *74*, 802–812.

Miyazaki, M., & Morita, N. (2005). Effect of heat–moisture treated maize starch on the properties of dough and bread. *Food Research International*, *38*, 369–376.

Pinto, V. P., Vanier, N. L., Klein, B., Zavareze, E. R., Elias, M. C., Gutkoski, L. C., et al. (2012). Physicochemical, crystallinity, pasting and termal properties of heat–moisture-treated pinhão starch. *Starch/Stärke*, *64*, 855–863.

Pukkahuta, C., Suwannawat, B., Shobsngob, S., & Varavinit, S. (2008). Comparative study of pasting and thermal transition characteristics of osmotic pressure and heat–moisture treated corn starch. *Carbohydrate Polymers*, *72*, 527–536.

Rabek, J. F. (1980). Applications of wide-angle X-ray diffraction (WAXD) to the study of the structure of polymers. In *Experimental methods in polymer chemistry* (1st ed., pp. 505–508). Chichester: Wiley-Interscience.

Varatharajan, V., Hoover, R., Jihong, L., Vasanthan, T., Nantanga, K. K. M., Seetharaman, K., et al. (2011). Impact of structural changes due to heat–moisture treatment at diferente temperatures on the susceptibility of normal and waxy potato starches towards hydrolysis by porcine pancreatic alpha amylase. *Food Research International*, *44*, 2594–2606.

Vermeylen, R., Goderis, B., & Delcour, J. A. (2006). An X-ray study of hydrothermally treated potato starch. *Carbohydrate Polymers*, *64*, 364–375.

Wang, L., & Wang, Y. J. (2004). Rice starch isolation by neutral protease and high-intensity ultrasound. *Journal of Cereal Science*, *39*, 291–296.

Watcharatewinkul, Y., Puttanlek, C., Rungsardthong, V., & Uttapap, D. (2009). Pasting properties of a heat–moisture treated canna starch in relation to its structural characteristics. *Carbohydrate Polymers*, *75*, 505–511.

Zavareze, E. R., & Dias, A. R. G. (2011). Impact of heat–moisture treatment and annealing in starches: A review. *Carbohydrate Polymers*, *83*, 317–328.

Zavareze, E. R., Storck, C. R., Castro, L. A. S., Schirmer, M. A., & Dias, A. R. G. (2010). Effect of heat–moisture treatment on rice starch of varying amylose content. *Food Chemistry*, *121*, 358–365.